OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0474

Technical Report No. 3

SENSITIVITY OF POLYMER BLENDS TO SYNCHROTRON RADIATION

by

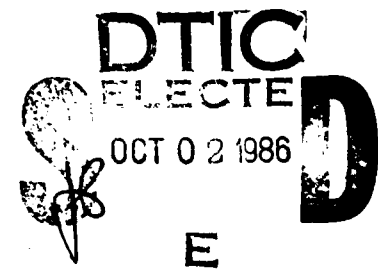J. A. Jubinsky, R. J. Groele, F. Rodriguez,
Y. M. N. Namaste, and S. K. Obendorf

Olin Hall, Cornell University
School of Chemical Engineering
Ithaca, NY 14853

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 3	**2. GOVT ACCESSION NO.** AD-A172 802	**3. RECIPIENT'S CATALOG NUMBER**
4. TITLE (and Subtitle) SENSITIVITY OF POLYMER BLENDS TO SYNCHROTRON RADIATION		**5. TYPE OF REPORT & PERIOD COVERED** Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. A. Jubinsky, R. J. Groele, F. Rodriguez, Y. M. N. Namaste, and S. K. Obendorf		**8. CONTRACT OR GRANT NUMBER(s)** N00014-85-K-0474
9. PERFORMING ORGANIZATION NAME AND ADDRESS Cornell University Ithaca, NY 14853		**10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS**
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Office of Naval Research Arlington, VA 22217		**12. REPORT DATE** September 26, 1986
		13. NUMBER OF PAGES 22
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		**15. SECURITY CLASS. (of this report)** Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Technical Report Distribution List, GEN/413-2.
For unlimited distribution and public release.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Abstracts Distribution List, 356A/413-2.
For unlimited distribution and public release.

18. SUPPLEMENTARY NOTES

Presented at the American Chemical Society meeting (Div. Of Polymeric Materials: Sci. & Eng.), Anaheim, CA, Sept. 5-12, 1986

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Microlithography
X-ray lithography
Polymer blends
Synchrotron radiation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The sensitivity of poly(methylmethacrylate), PMMA, to x-rays is enhanced by the addition of poly(epichlorohydrin), CO rubber. The two polymers appear to be miscible over a wide concentration range. Films with 20 to 50% CO in PMMA require only 1/2 to 1/4 the exposure dose of synchrotron radiation to produce an equivalent pattern in PMMA alone. The sensitivity is confirmed by measurements of molecular weight of blends irradiated by gamma rays or electrons, a well as x-rays. Dissolution behavior of the blends also is similar to that for PMMA.

DD FORM 1 JAN 73 **1473** EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SENSITIVITY OF POLYMER BLENDS TO SYNCHROTRON RADIATION

J.A. Jubinsky, R.J. Groele, and F. Rodriguez

School of Chemical Engineering, Olin Hall

Y.M.N. Namaste' and S.K. Obendorf

Dept. of Textiles and Apparel, Martha Van Rensselaer Hall

Cornell University, Ithaca, NY 14853

INTRODUCTION

When the resolving power of photolithography is to be ex-
ceeded, the two technologies that are most often called upon are
electron-beam and x-ray lithography. For purposes of discussion,
the lower limit of features using optical (deep UV) methods may be
placed at about 0.5 μm. Electron beams currently can be used to
produce features from 1.0 to 0.5 μm. Since backscattering is not
a problem, the minimum dimensions obtainable with x-rays in deep
films may well be smaller than those obtained with electron beams.
Moreover, x-ray lithography is efficient for large volume produc-
tion of chips. Electron-beam technology has been widely used for
some time in mask-making and for customized, low-volume chip pro-
duction, so a considerable body of information has been acumulated
on the response of polymers to 20- to 50-keV electrons. A similar
body of information does not exist on the response to x-rays.

There are currently three types of x-ray sources available to
researchers: anodic, in which high-energy electrons act on a
metal target; plasma, in which IR or UV laser radiation acts on a
metal target; and synchrotron, in which a beamline is attached to

a high-energy electron storage ring. Anodic sources are the least expensive type, but they are from 100 to 10,000 times less intense than the other sources. As source strength is increased and exposure times reduced, sensitivity is a less urgent matter. When the response of a given resist to x-rays is being measured, the wavelength of the radiation has to be taken into account also. While synchrotron radiation is intense, the energy distribution may not be concentrated in the regions corresponding to efficient absorption by the atoms making up the resist.

Several reports have been published on x-ray resists in recent years. Haelbich et al. (1) compared the performance of PMMA using synchrotron radiation with that using e-beam radiation. Yaakobi (4) et al. used a laser-ion x-ray source. The general topic of x-ray resists has been reviewed by Lane (3) and Taylor (4). A very optimistic view of the future for synchrotron-based lithography was taken by Wilson (5). More guarded predictions of eventual application of x-rays have been made by Broers (6) and Heuberger (7).

Poly(methylmethacrylate), (PMMA), is one resist which is especially favored by researchers due to its high resolution and contrast (γ = 2 to 3). Linewidths as small as 100 $\overset{o}{A}$ have been produced with an extremely high dose (10 J/cm^2) using PMMA. However, even PMMA's normal sensitivity of 600-1000 mJ/cm^2 is too slow for commercial use. There have been many attempts to improve the sensitivity of PMMA to electron beam irradiation mainly by copolymerization (8). In the current paper, we describe an alternative approach whereby a sensitive polymer is physically blended

with PMMA to increase its sensitivity and yet maintain the good film qualities associated with PMMA as a positive x-ray resist.

Poly(epichlorohydrin), CO rubber* (Hydrin^R), was chosed for various reasons. The main reason was that CO has been shown to be miscible with PMMA by Anderson based upon differential scanning calorimetry (DSC) which showed only one glass transition tempera-ture (T_g) for the blend (9). Since T_g is very sensitive to the disruption of the local structure that results when two polymers are mixed, the existence of a single glass transition temperature is a good indicator of miscibility (10). CO contains chlorine which tends to enhance x-ray absorption especially near the ab-sorption edge of 4.4 Å. It was hoped that the increase in absorp-tion would produce more secondary electrons which would in turn increase the sensitivity of PMMA.

Our exploratory work indicated that CO degrades rapidly on gamma radiation. Taylor et al. (11), using a very high molecular weight CO, has reported that CO crosslinks appreciably when exposed to $Pd_{L\alpha}$ x-rays. In the present work no decrease in solu-bility has been observed and only a very slight broadening of the molecular weight distribution.

EXPERIMENTAL PROCEDURE

CO rubber (Hydrin 100) was obtained from the B.F. Goodrich Chemical Company. Based upon gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a carrier solvent, the CO has a

---

*ASTM abbreviation for this polymer.

polystyrene equivalent number average molecular weight (M_n) of 303×10^3 and weight average molecular weight (M_w) of 598×10^3. DSC results by Anderson showed that it has a glass transition temperature of -20°C (9). The PMMA used was Rohm and Haas A-100 with M_n of 113×10^3 and M_w of 213×10^3.

Three mixtures of CO-PMMA were blended together for analysis of lithographic performance. Compositions of 20, 33, and 50% CO by weight were blended by dissolution in THF to form a 13% (total solids) solution. Cyclohexanone was added to the blend to form a 7% solution to impart proper viscosity and volatility for casting films. In the case PMMA with $M_n = 950 \times 10^3$, CO was dissolved in hot chlorobenzene and then mixed with PMMA (also in chlorobenzene).

The films were spun at 1250 RPM for 1 minute on three-inch silicon wafers. The wafers were baked at 150°C for 1 hour in a forced-convection air oven. Film thicknesses ranged between 0.8 and 1.3 micrometers. PMMA samples were also prepared using the same casting solvent mixture and baking conditions.

Gel permeation chromatography was used to determine polymer molecular weights. The model used was a Waters Associates 201 HPLC with 4 μStyragel columns (nominal pore sizes of 500, 10^3, 10^4, and 10^5 Å). THF was used as the carrier solvent. The molecular weights were reported as polystyrene equivalents with the exception of PMMA for which a PMMA calibration standard was used.

Glass transition temperatures (T_g) were measured using a Perkin Elmer Differential Scanning Calorimeter (DSC) model DSC-2C. DSC measures glass transition temperatures by supplying energy to

the sample and to a reference to keep them both at the same temperature. At the glass transition temperature, there is a change in the specific heat of the sample. This causes a change in the amount of heat required to keep the sample and the reference at the same temperature. This will show up as a step change in the baseline of a heat supplied versus temperature curve.

The x-ray exposures were carried out using synchrotron radiation delivered by the National Synchrotron Light Source at Brookhaven National Laboratories. The beamline was built by IBM and has been described elsewhere (12,13). In summary, the storage ring operates with electron energies at 750 MeV and a magnetic radius of 1.91 meters. The current in the ring, which degrades with time, ranges between 75 and 250 mA. The actual power through the beryllium window and incident on the wafer ranged from 2.3 to 7.5 mW/cm^2 in the present work. Samples were exposed to synchrotron radiation through a gold-on-boron nitride mask and then developed using various mixtures of isopropyl alcohol (IPA) and methyl isobutyl ketone (MIBK). Development was conducted under stirred conditions using a constant temperature bath at 23°C and was terminated by blow drying with compressed air. Film thicknesses were measured by a Tencor Alpha Step.

Electron beam exposures were performed using a modified RCA model EMV-3 transmission electron microscope. The aperture was opened to allow the beam to spread out over an entire 3-inch wafer to give uniform exposure. The accelerating voltage was 50 keV, and the dose was measured using a faraday cup.

Gamma radiation was carried out in Cornell's Ward Reactor Laboratory. Using ^{60}Co, rates of about 0.5 Mrad/hour can be achieved. Bulk, rather than film, samples were used. They were held in nitrogen-purged test tubes during exposure.

Laser interferometry was used to study the dissolution rate of some of the films used in this work (14,15). A 632.8 nm wavelength beam of unpolarized light from a 2 mW He-Ne laser is directed on a submerged wafer coated with a polymer film. The angle of incidence is approximately 10°. Reflected light from the polymer-solvent and polymer-substrate interfaces is directed toward a photocell which is coupled to a chart recorder. As the polymer solvent interface begins to recede due to dissolution, constructive and destructive interference from the interface takes place, and a sinusoidal output is recorded. By measuring the period of the sinusoidal curve, the dissolution rate can be determined.

RESULTS AND DISCUSSION

Lithographic performance of the CO-containing samples was evaluated by constructing contrast and thinning curves. Contrast curves were constructed by measuring the dissolution rate for various doses and arbitrarily chosen development times. Typical contrast curves are shown for the 33% CO blend and for the PMMA (Figure 1). From the contrast curves, thinning curves were constructed by plotting the unexposed normalized thickness remaining versus the dose required for complete development (Figure 2).

The thinning curves show that the 33% CO blend is more sensitive than PMMA. However, the contrast of the blend is somewhat

reduced. Resist contrast is very important in x-ray lithography because mask contrast tends to be low. This is due to the fact that the most absorbing materials such as gold are only about a factor of 50 higher in their absorption coefficients than the most transparent. In comparison, optical contrast can be as high as 10^{10}. Poor resist contrast in conjunction with the inherently poor mask contrast will result in increased thinning and sloping sidewalls. The gold on boron nitride mask used in the present work (see below), for example, had an effective ratio of 10:1 for intensity in the open versus the masked areas.

Referring to Figure 2, there is a trend toward increasing sensitivity as the percentage of CO is increased indicating that CO imparts its good sensitivity to the blend. For example, at 20% thinning, the dose required to completely develop the 33 and 50% CO blends are 2 and 3 times less, respectively, than that needed for PMMA. However, this occurs at the expense of contrast which is reduced by 25 to 40 percent. Furthermore, as the allowable percentage of thinning is reduced, the difference in sensitivity narrows. This is discussed later. One does not notice any trend with respect to contrast among the CO blends. The 33% blend appears to have the best contrast, but it is still significantly lower than that of the PMMA.

The mechanism behind the increase in the sensitivity of the blend appears to involve the scissioning and dissolution properties of CO. At low concentrations, CO initially speeds up the development rate of the blend as compared to PMMA. However, as the concentration of the CO is increased (between 20 and 33%), the

dissolution rate does not increase as rapidly. When the blend is exposed to radiation, the CO scissions and its molecular weight is decreased. The decrease in molecular weight behaves as if one was decreasing the percentage of CO in the blend which results in the enhancement of the dissolution rate. This was confirmed by utilizing a lower molecular weight (M_n = 86 x 10^3) CO sample obtained by gamma irradiation. A 33% by weight CO blend using the low molecular weight CO sample was spin coated under the same conditions as previously described. The dissolution rate of this unexposed blend was about 8 times faster than an unexposed higher molecular blend (using a 45% IPA-MIBK development mixture). Thus, the increase in the dissolution rate between the exposed and unexposed regions appears to be primarily due to the scissioning of the CO. This accounts for the increase in sensitivity.

At high doses, the ability of the CO to influence the dissolution rate is diminished since its absolute molecular weight is no longer changing significantly. It appears that the main mechanism for increasing dissolution at higher doses is not due to the degradation of the CO, but the scissioning of the PMMA. This accounts for the apparent similarity in behavior of PMMA and the blends at high doses. Thus, the increased sensitivity of the blends is realized only in the "forced developing" regimes.

The relative response of CO/PMMA blends to various forms of radiation can be compared. In the first place, gamma radiation of bulk samples of CO or PMMA results in values of G(s) = 5.1 scissions/100 eV for CO compared to 0.8 for PMMA (Figure 3). It is not so surprising that a rubbery polymer like CO should have a

high sensitivity. It is interesting that the structure leads pri-
marily to scissioning with little crosslinking (G(x) = 0.5 at
most). It is presumably the ether linkage in combination with the
substituted chain carbon which leads to scission. Poly(ethylene
oxide), in contrast, crosslinks readily, even in dilute solution
as long as oxygen is excluded (16). Taylor (11) found that the
disubstituted homolog, poly(cis-1,2-dichloromethyloxirane), was
unequivocally a scissioning compound, but that CO appeared to
crosslink somewhat. As mentioned earlier, this may have been due
to the higher molecular weight CO which he employed.

Sensitivity of CO to electrons and x-rays was characterized
by comparing a blend with PMMA to PMMA alone. In a beam of 50 keV
electrons, a blend of CO to PMMA in the ratio 1:2 exhibits a slope
about 2.9 times that of PMMA (Figure 4). However, the polydisper-
sity, M_w/M_n, of the blend (shown on the same plot) reflects the
fact that the CO is degrading faster than the PMMA. The polydis-
persity of neat PMMA remains between 1.9 and 2.3 under the same
experimental conditions.

Synchrotron radiation yields a similar pattern to the e-beam
result when the same blend and PMMA are compared (Figure 5). Once
again, the slope for the blend is about 2.7 times the slope for
PMMA.

Chlorine might be expected to enhance the sensitivity to
x-rays over that to gamma radiation or electrons. The present
work does not demonstrate the effect. The most probable reason is
that the synchrotron beam was operating under conditions where the
~~energy~~ *intensity* was not high at the absorption edge for chlorine (4.4Å).

The dissolution behavior of CO-PMMA blends was examined for two molecular weights of PMMA (Table 1):

Table 1. Dissolution in MIBK, 30°C

M_n of PMMA	PMMA alone		CO:PMMA, 1:4	
	Diss. Rate	f**	Diss. Rate	f
360×10^3	0.031	0.80	0.27	0.61
29×10^3	0.14	0.97	0.75	0.94

In each case, the dissolution rate was increased by addition of CO. Two additional features can be noted. The amplitude of the oscillations in reflected light intensity appears to remain constant as the blends dissolve. This would indicate that the undissolved portion of the film is not undergoing swelling or extraction to any noticeable extent. The second feature, observable especially in the high molecular weight PMMA blend, is an increased offset between the maximum amplitude during dissolution and the reflection from the bare wafer after dissolution is complete (Figure 6). This offset has been interpreted as representing a transition layer on the surface of the dissolving film (17).

**Oscillation amplitude reduction factor (17), $f = (a - b)/(a - b + 2s)$, where a and b are maximum and minimum reflected light intensities during dissolution and s is the offset (Figure 6).

The increase in the offset means that the CO-PMMA blend has a thicker surface layer. On the other hand, the fact that the offset is only very slightly increased by high molecular weight CO with the lower molecular weights of PMMA means that the transition layer is probably not due to entangled CO molecules remaining on the surface.

Despite the rather low contrast available with a 1:2 blend of CO:PMMA, 0.5 μm lines and 0.3 μm spaces were developed with a dose of 400 mJ/cm^2 (Figure 7). Comparable resolution with PMMA would require a little over twice that dose.

CONCLUSIONS

The sensitivity of PMMA can be increased by adding CO as a blend. The sensitivity of the blend in comparison to the PMMA increases under more forced developing conditions (i.e. longer developing times for development of lower doses). However, under severe conditions, the contrast of the blends suffers greatly which would make it difficult to form good lithographic patterns. At 15 to 20% thinning, the 33 and 50% CO by weight blends still show a 2- to 3-fold increase in sensitivity over that of PMMA. However, this occurs at the expense of a 25 to 40% reduction in contrast.

The mechanism behind the increase in sensitivity is that at significantly high concentrations the CO acts as a dissolution inhibitor. Upon irradiation, the molecular weight of the CO decreases which enhances the dissolution of the blend.

ACKNOWLEDGMENTS

Literature Cited

1. Haelbich, R.P., et al. J. Vac. Sci. Tech. 1983, B1(4), 1072.

2. Yaakobi, B., et al., Applied Physics Letters, 1983, 43, 686.

3. Lane, J.G., Adv. Resist Tech. and Proc. 1983.

4. Taylor, G.N., Solid State Tech. 1980, 23(5), 73.

5. Wilson, A.D., Solid State Tech. 1986, 29(5), 249.

6. Broers, A.N., Solid State Tech. 1985, 28(6), 119.

7. Moreau, W.M., Optical Engineering 1983, 22(2), 18.

8. Heuberger, A., Solid State Tech. 1986, 29(2), 93.

9. Anderson, C.C., Rodriguez, F., Proc. ACS Div. Polym. Matls.: Sci. & Eng. 1984, 51, 609.

10. Olabisi, O., in Encyclo. Chem. Tech. 3rd ed., Wiley, New York, 1982, Vol. 18, p. 443.

11. Taylor, G.N., Coquin, G.A., Somekh, S., Polym. Eng. Sci., 1977, 17, 420.

12. Silverman, J.P., Haelbich, R.P., Grobman, W.D., Warlaumont, J.M., Proc. SPIE Vol. 393, 1983.

13. Haelbich, R.P., Silverman, J.P., Warlaumont, J.M., Nuc. Inst. Meth., 1984, 222, 291.

14. Rodriguez, F., Krasicky, P.D., Groele, R.J., Solid State Tech., 1985 28(5), 125.

15. Rodriguez, F., Groele, R.J., Krasicky, P.D., Adv. Resist Tech. Proc., 1985, 539, 14.

16. van Brederode, R.A., Rodriguez, F., Cocks, G.G., J. Appl. Polym. Sci., 1968, 12, 2097.

17. Krasicky, P.D., Groele, R.J., Jubinsky, J.A., Rodriguez, F.,

14

Namaste, Y.M.N., Obendorf, S.K., <u>Proc. 7th Int. Conf. on Photopolymers, SPE</u>, 1985, p. 237.

Figure Captions

1. Contrast curves for x-ray, flood-exposed films developed one minute in indicated mixtures of isopropyl alcohol and methyl isobutyl ketone,(a) PMMA and b) CO:PMMA, 1:2.

2. Thinning curves for PMMA and various blends containing (a) 50%, (b) 33%, (c) 20%, and (d) 0% CO by weight. The numbers in parentheses give the fraction of isopropyl alcohol in the solvent (balance is MIBK). The gamma value (contrast) also is given.

3. Sensitivity to gamma radiation (Cobalt source) for (a) CO, $G(s) = 5.1$, and (b) for PMMA, $G(s) = 0.8$.

4. Sensitivity to 50 keV electrons for (a) PMMA and (b) CO:PMMA, 1:2. The slope for the blend is 2.9 times that for PMMA.

5. Sensitivity to x-rays (flood exposure through berylium window) for same materials as in figure 4. The slope for the blend is 2.7 times that for PMMA. Polydispersity for PMMA ranges from 1.9 to 2.3 at all doses.

6. Dissolution rates measured by interferometry using MIBK at 30°C for (a) high molecular weight PMMA and (b) CO:PMMA, 1:4.

7. Pattern in CO:PMMA, 1:2. Conditions were 400 mJ/cm^2 synchrotron radiation through gold on boron nitride mask. Developed in MIBK-IPA mixture.
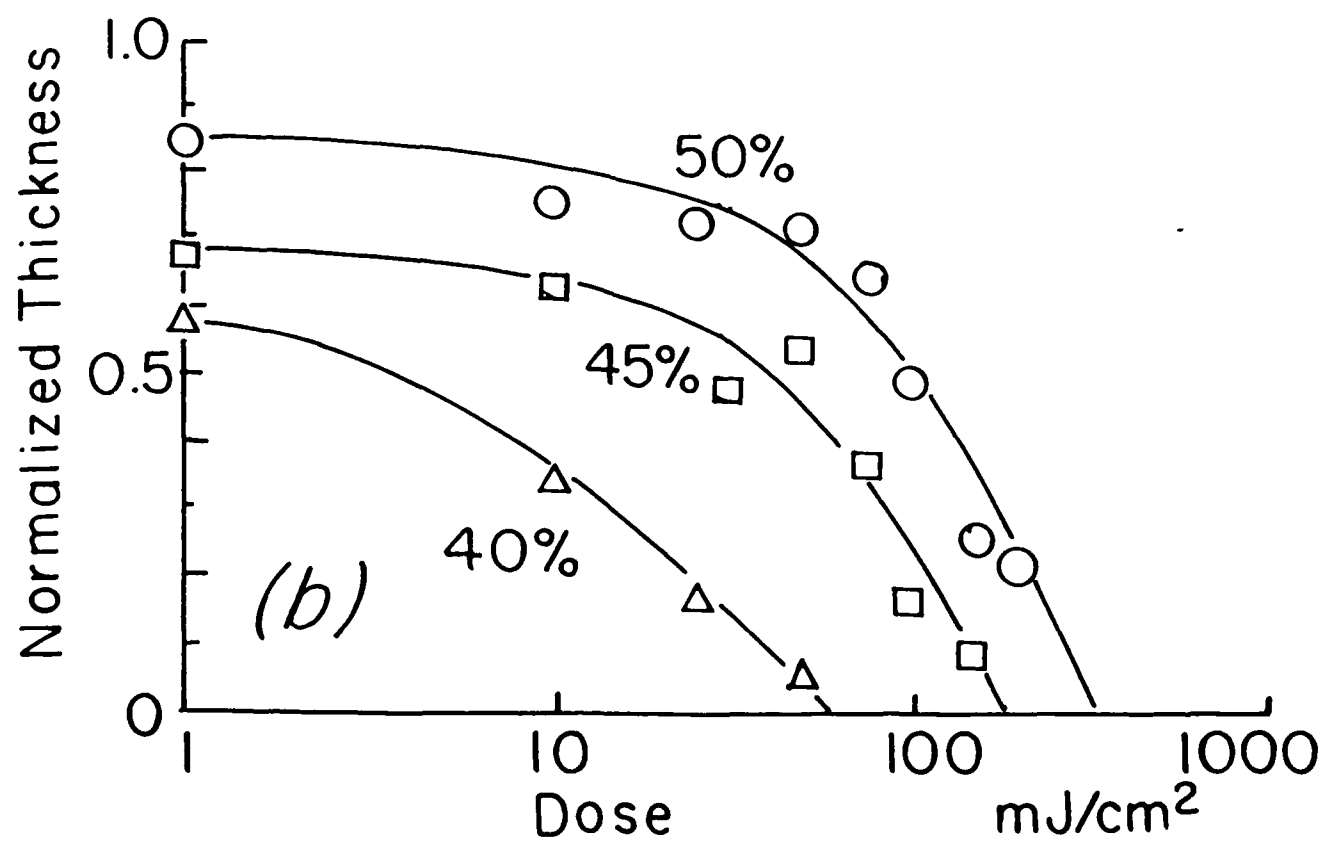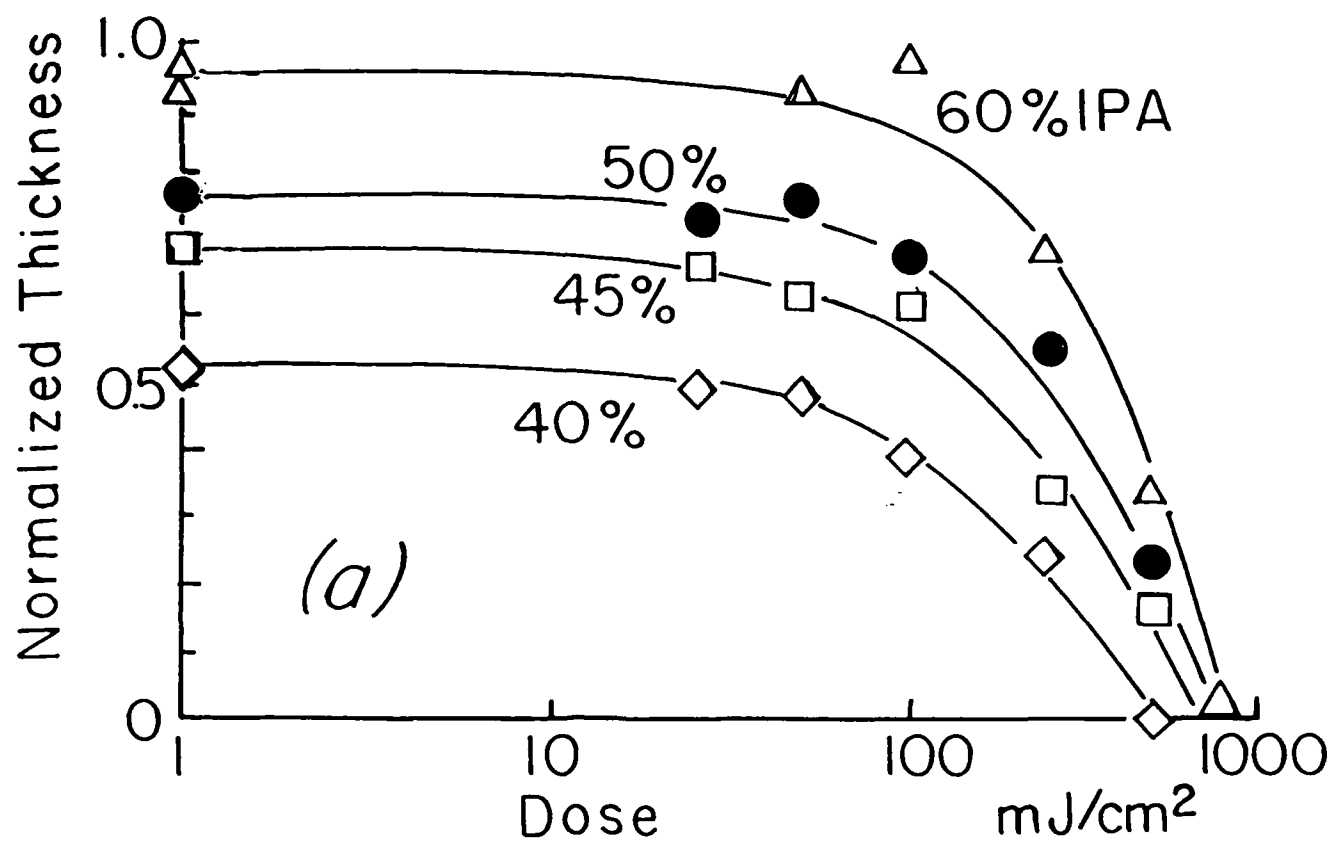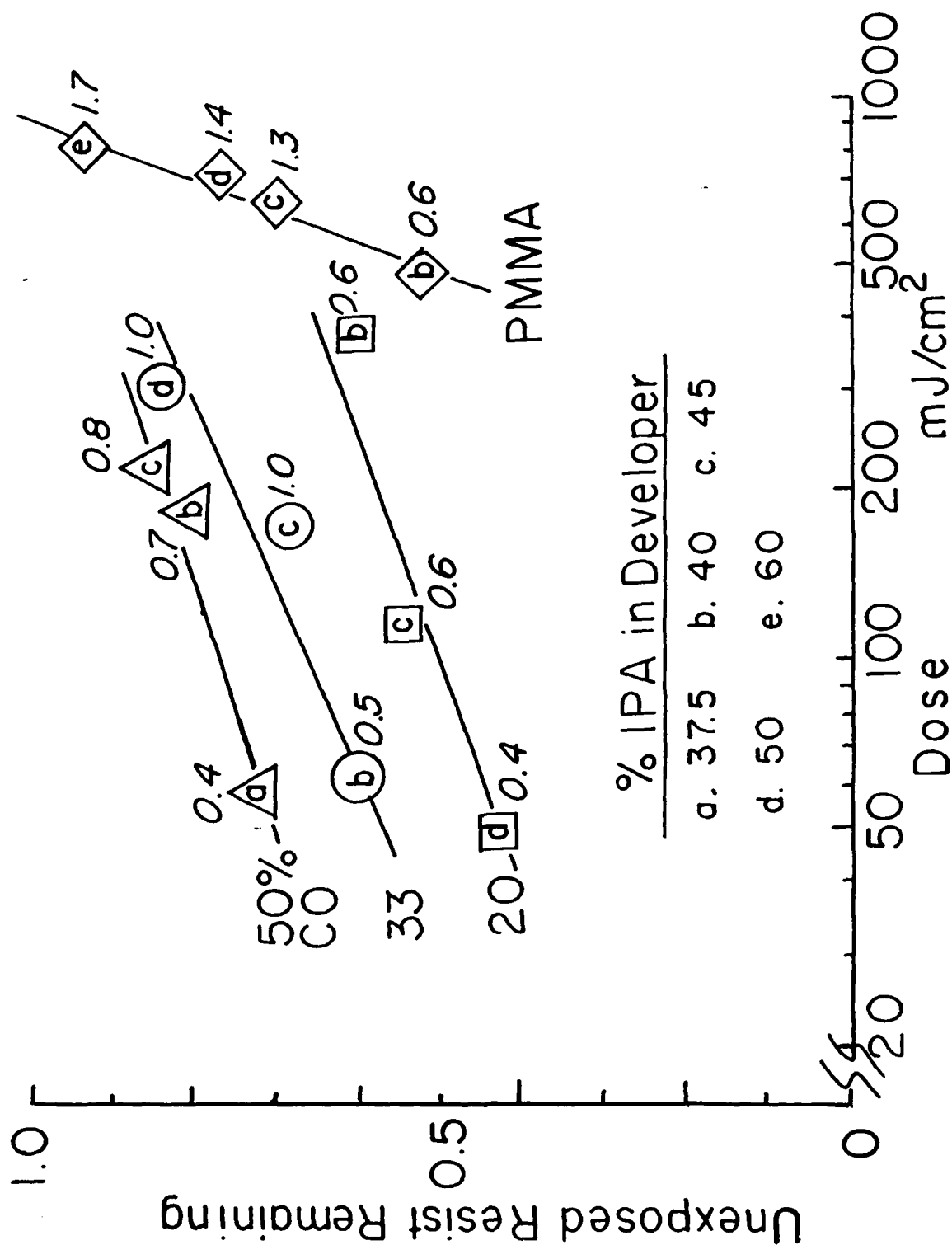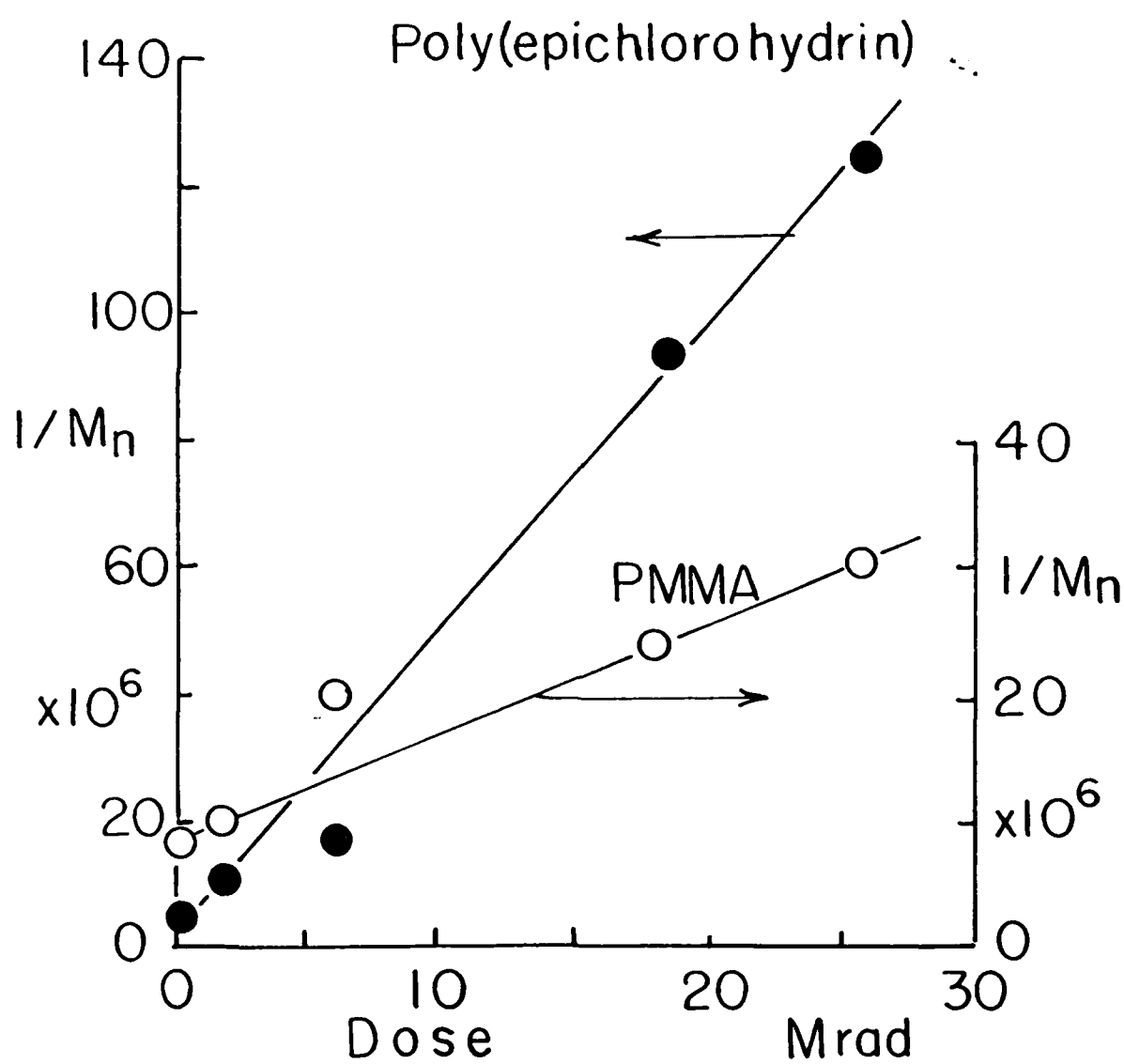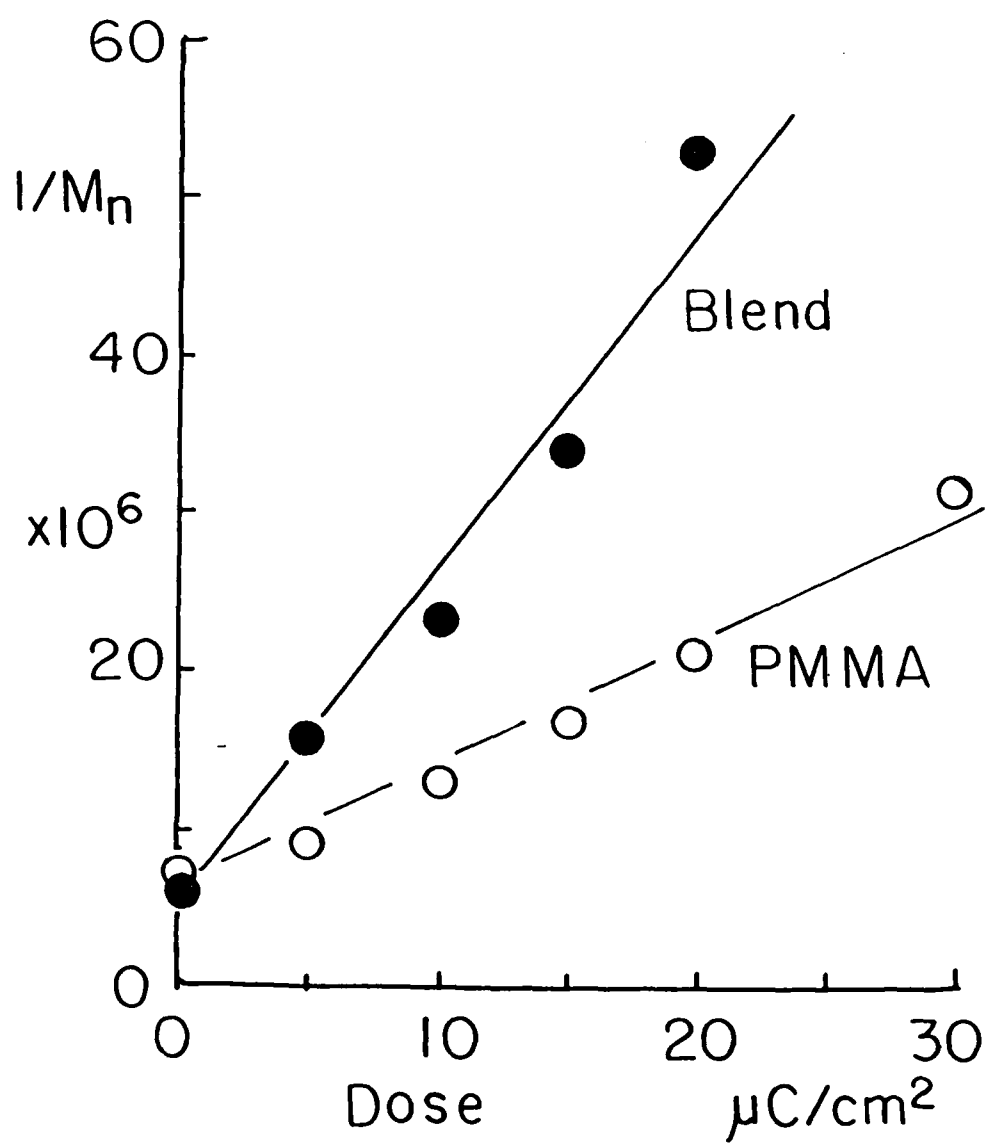
Fig. 1

Fig. 2

Fig. 3

Fig. 4
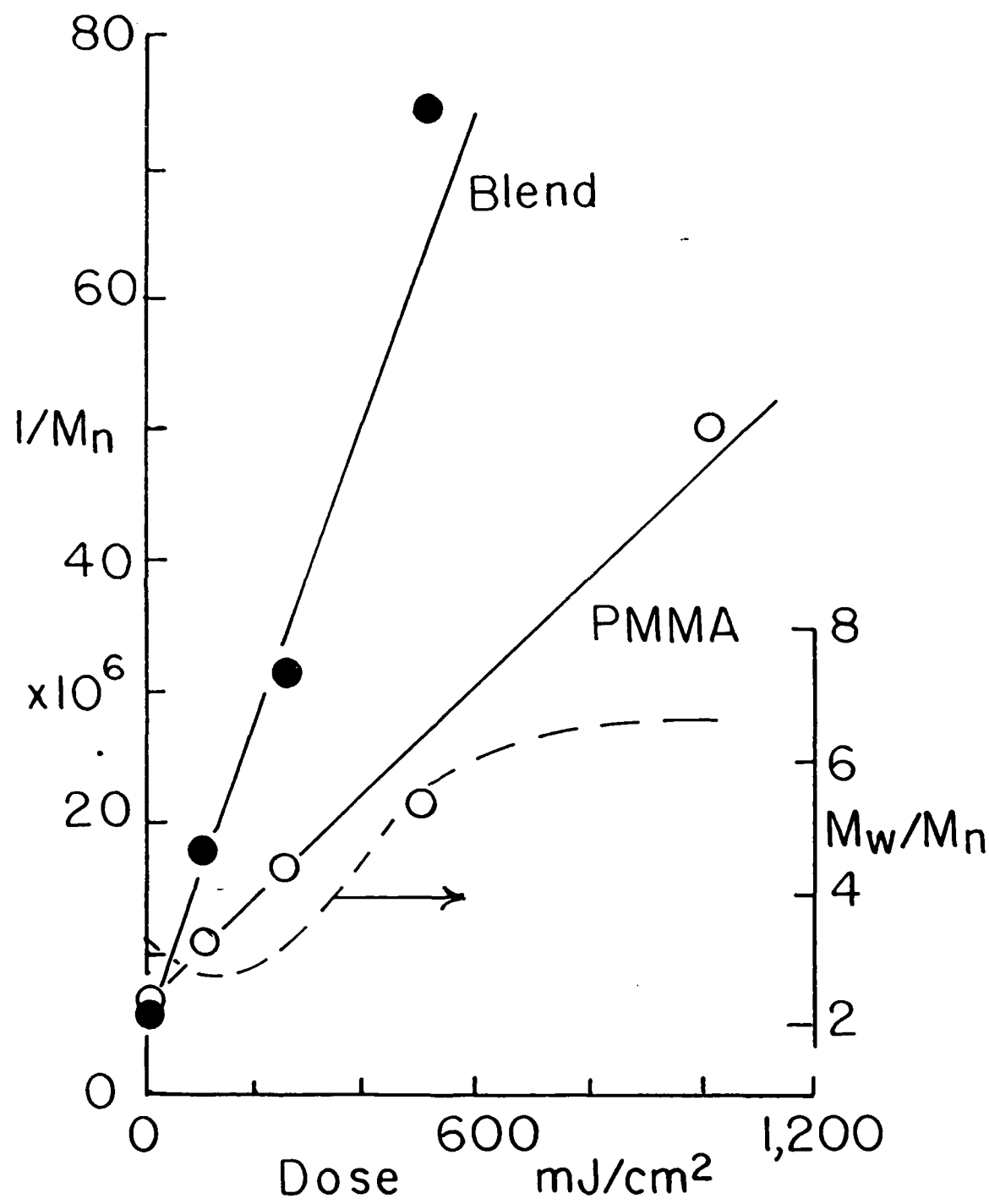
Fig. 5
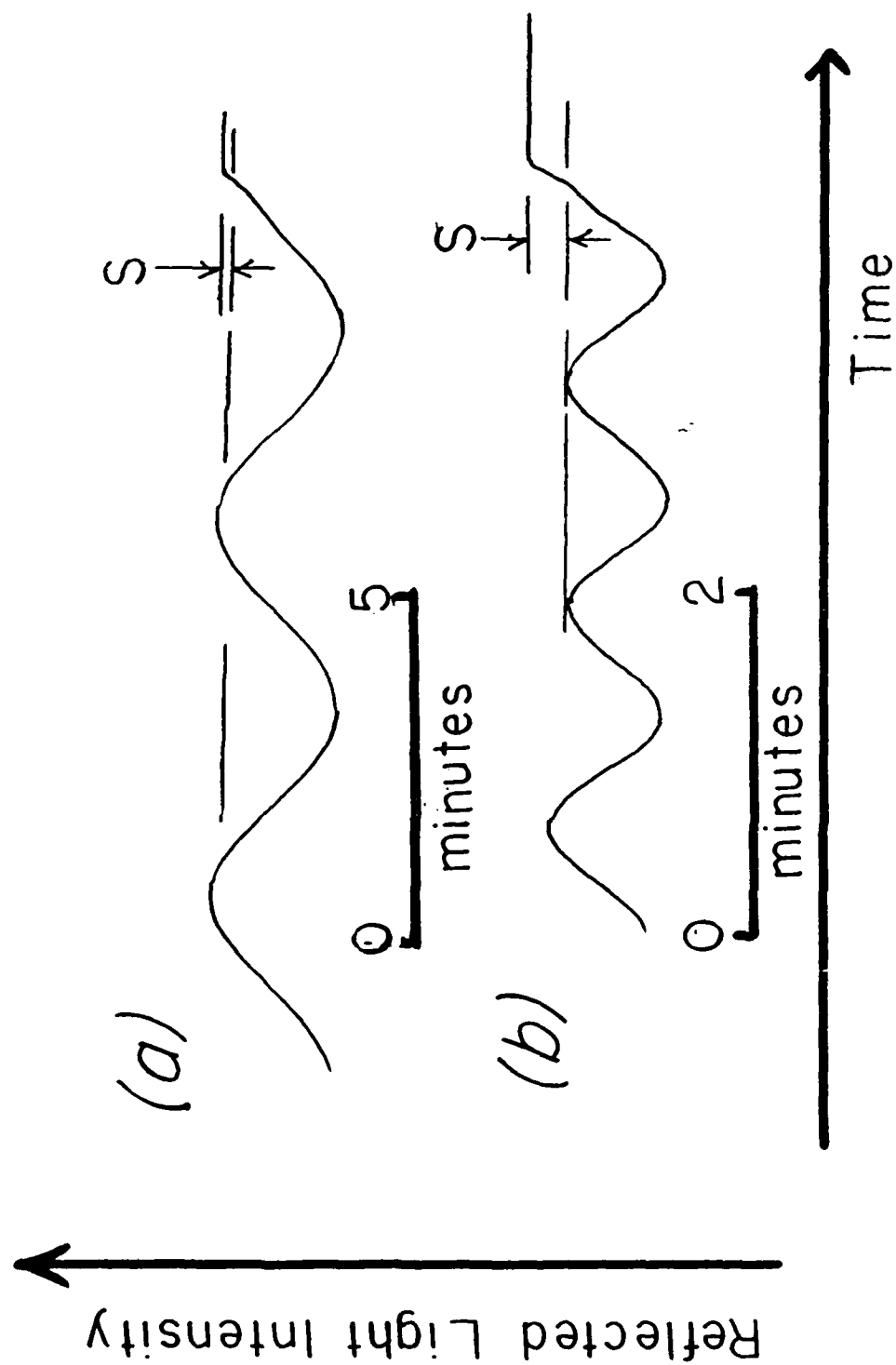
Fig. 6
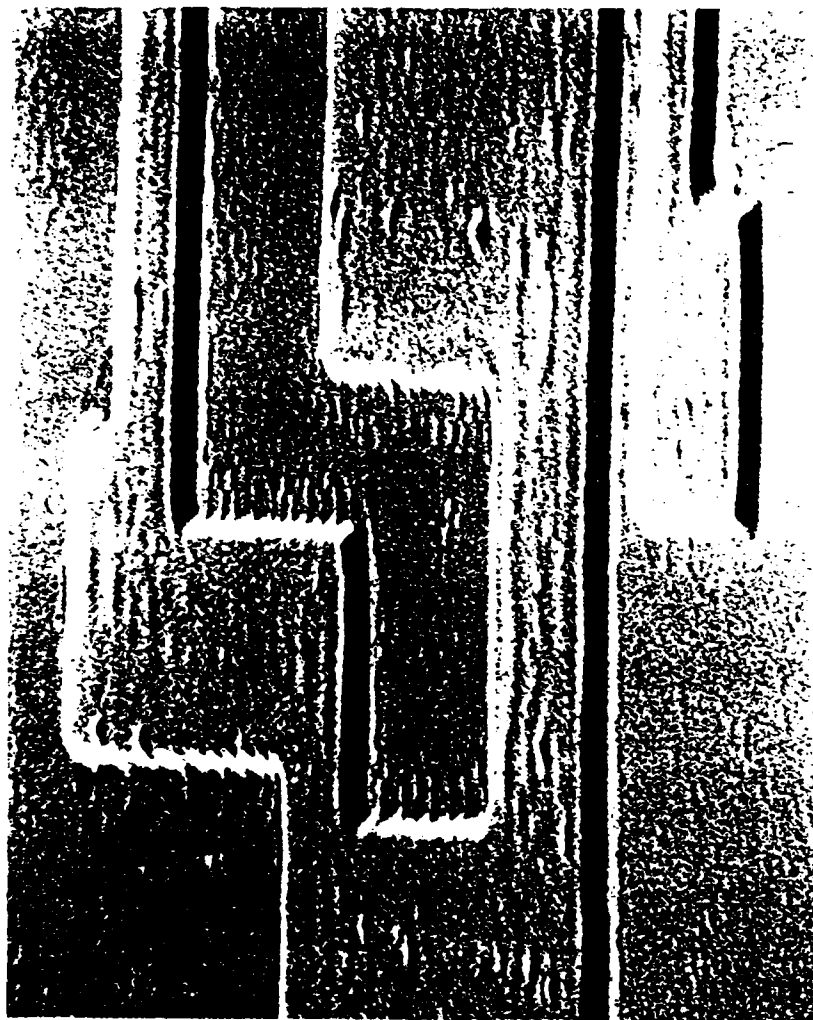
$1 \mu m$

Fig. 7

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies		No. Copies
Office of Naval Research Attn: Code 413 800 N. Quincy Street Arlington, Virginia 22217	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 5042 Crane, Indiana 47522	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
DTNSRDC Attn: Dr. G. Bosmajian Applied Chemistry Division Annapolis, Maryland 21401	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1		

END

11-86

DTIC